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(71) Applicant: SUMITOMO ELECTRIC INDUSTRIES, LIMITED
5-33, Kitahama 4-chome
Chuo-ku
Osaka(JP)

(72) Inventor: Tsuno, Takashi, c/o Itami Works of Sumitomo
Electric Ind., Ltd.,
1-1, Koyakita 1-chome
Itami-shi, Hyogo(JP)
Inventor: Imai, Takahiro, c/o Itami Works of Sumitomo
Electric Ind., Ltd.,
1-1, Koyakita 1-chome
Itami-shi, Hyogo(JP)
Inventor: Fujimori, Naoji, c/o Itami Works of Sumitomo
Electric Ind., Ltd.,
1-1, Koyakita 1-chome
Itami-shi, Hyogo(JP)

(74) Representative: Kirschner, Klaus Dieter, Dipl.-Phys.
Patentanwälte
Herrmann-Trentepohl, Kirschner, Grosse, Bockhorni & Partner
Forstenrieder Allee 59
D-81476 München (DE)

(54) Epitaxial growth of diamond from vapor phase.

(57) A plurality of single-crystalline diamond plates (52) having principal surfaces consisting essentially of {100} planes are prepared. The plurality of single-crystalline diamond plates (52) are so arranged that the respective principal surfaces are substantially flush with each other. At this time, an angle formed by crystal orientations in relation to the principal surfaces between adjacent plates (52) is not more than 5°, a clearance between the adjacent plates is not more than 30 μm, and difference in height in relation to the principal surfaces is not more than 30 μm between the adjacent plates. In order to fix such a state, it is possible to join the plurality of diamond plates with each other by depositing diamond on these plates. After such joining, the principal surfaces of the diamond plates are polished in order to eliminate steps. Then, diamond is epitaxially grown on a polished surface of a large diamond plate (53) which is formed by the plurality of diamond plates (52) from a vapor phase. In this vapor phase, proportions A, B and C obtained from the following equations I, II and III respectively satisfy the following conditions:

$0.5 \leq A \leq 2.0$
$0.3 \leq B \leq 2.0$
$C \leq 1.0$

$$A = ([C]/[H]) \times 100\ \% \qquad \mathrm{I}$$

$$B = ([C] - [O]/[H]) \times 100\ \% \qquad \mathrm{II}$$

$$C = ([O]/[H]) \times 100\ \% \qquad \mathrm{III}$$

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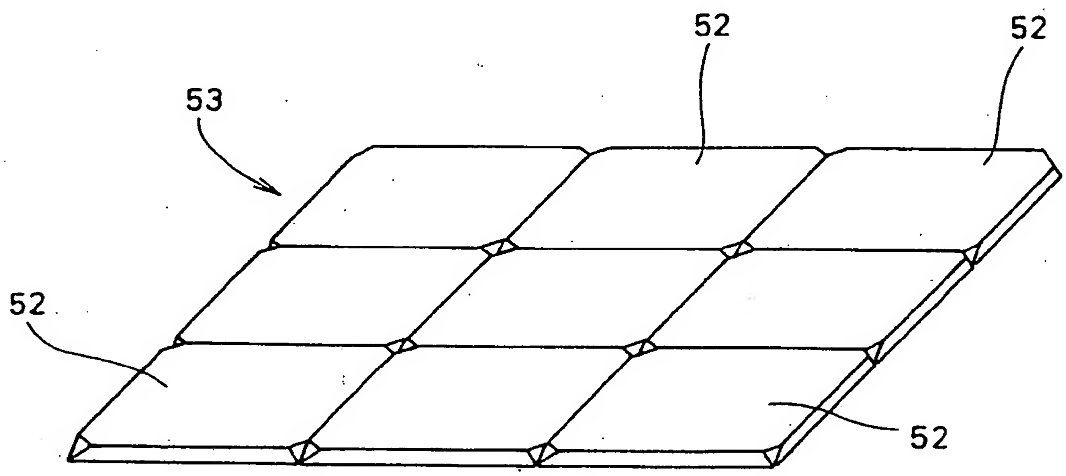
where [C], [O] and [H] represent molar numbers of carbon, oxygen and hydrogen atoms respectively. According to this method, it is possible to obtain vapor-deposited diamond which exhibits a maximum diameter of at least 15 mm, transmittance of at least 20 % with respect to ultraviolet light of 250 nm in wavelength, and a peak having an angular half-width of not more than 100 seconds in an X-ray rocking curve in a (400) plane or a half-width of not more than 2 cm^{-1} at 1332 cm^{-1} in a Raman scattering spectrum.

FIG. 9C



BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to vapor-deposited diamond and a method of producing the same, and more particularly, it relates to a technique for providing a large diamond single crystal which is applied to a semiconductor material, an electronic component, an optical component or the like.

Description of the Background Art

Diamond, which has a number of excellent properties such as high hardness, high thermal conductivity, high light transmittance and a wide band gap, is widely applied to a material for a tool, an optical component, a semiconductor device or an electronic component, and its importance may be further increased in the future.

Single crystals of natural diamond include that called a type IIa diamond single crystal which transmits ultraviolet light of up to 230 nm and that called a type Ia diamond single crystal which hardly transmits ultraviolet light. In either case, it is extremely difficult to obtain a natural single crystal of at least 10 mm in diameter. Although single-crystalline diamond which is close to 20 mm in diameter is rarely naturally produced, such diamond is too high-priced for an industrial use. Natural type IIa diamond has a large amount of crystal defects and distortion. Such natural IIa diamond is regarded as being unsuitable to a substrate for a semiconductor device, since the same has an angular half-width of at least 500 seconds in an X-ray rocking curve and a half-width of at least 2 cm^{-1} in a spectrum of Raman scattered light observed at around 1332 cm^{-1}. On the other hand, type Ia diamond is not applicable to an optical material for ultraviolet light, since the same transmits no ultraviolet light of not more than 300 nm.

While naturally produced diamond has been applied to an industrial use in the past, artificially synthesized diamond is mainly applied to such an industrial use at present. A diamond single crystal is industrially synthesized under a pressure of at least tens of 1000 atoms for stabilizing the same, at present. A superhigh pressure vessel for generating such a pressure is so high-priced that its content volume is hard to increase and diamond cannot be supplied at a low cost. In such a high-pressure method, therefore, synthesis of a large single crystal is limited. Further, diamond which is produced by the high-pressure method is easily converted to a crystal called a type Ib diamond crystal, which contains nitrogen as an impurity. The type Ib diamond is relatively large, while the same transmits absolutely no light of not more than 400 nm in wavelength. Thus, it has been impossible to artificially synthesize a diamond single crystal of at least 10 mm in diameter, which transmits ultraviolet light of around 250 nm.

On the other hand, vapor deposition can be listed as a method of synthesizing diamond, which has been established with the high-pressure method. It is possible to artificially produce diamond which has a relatively large area of several to 10 cm, while such diamond is generally in the form of a polycrystalline film. When a diamond film is formed by vapor deposition, a substrate is generally previously scratched with diamond grains. It is understood that an effect of promoting growth of a diamond film by scratching is attained due to fine particles of diamond which are left on the substrate to serve as seed crystals for growing diamond (S. Iijima, Y. Aikawa and K. Baba, Appl. Phys. Lett. 57 (1990), 2646). The diamond particles which are left on the substrate after scratching are directed to various orientations, and hence diamond grown from the particles, serving as seed crystals, forms a polycrystalline film. However, it is necessary to apply single-crystalline diamond to an ultraprecise tool, an optical component or a semiconductor device, which requires a smooth surface.

To this end, study has been made on a method of epitaxially growing single-crystalline diamond by vapor deposition. In general, epitaxial growth is classified into homoepitaxial growth of growing a target material on the same type of a substrate, and heteroepitaxial growth of growing a target material on different types of substrates. A single-crystalline substrate of a relatively large area can be easily obtained for the heteroepitaxial growth. At present, however, heteroepitaxial growth of diamond tends to cause a defect or distortion in the crystal, and is unsuitable to a method of obtaining a large-area diamond single crystal which is applied to an optical component or a semiconductor substrate. Therefore, it is still important to study homoepitaxial growth in order to produce a large-area diamond single crystal.

In relation to such homoepitaxial growth of diamond, various devices have been made in order to obtain large single crystals. Geis et al. have reported a method of arranging diamond particles of several 10 to 100 μm which may be applied to abrasive grains on a selectively etched Si substrate for growing diamond having a strong specific crystal orientation on this substrate (M. W. Geis, H. I. Smith, A. Argoitia, J. Angus, G. H. M. Ma, J. T. Glass, J. Butler, C. J. Robinson and R. Pryor, Appl. Phys. Lett., Vol. 58 (1991), p. 2485).

Japanese Patent Laying-Open No. 3-75298 (1991) and U. S. Patent No. 5,127,983 corresponding thereto disclose a method of arranging a plurality of single-crystalline diamond plates several mm square for growing diamond thereon from a vapor phase. According to this method, it is possible to obtain a large diamond crystal which can be regarded as a single crystal as to light transmittance and the like, although grain boundaries having extremely small inclinations may be present in boundaries between the substrates. In particular, it is disclosed that a practicable large diamond single crystal can be obtained by precisely controlling crystal orientations of and spaces between the plurality of diamond plates.

In order to obtain a diamond single crystal of at least 15 mm in size along the U. S. Patent, it is important to maintain homoepitaxial growth up to a prescribed thickness. While the U. S. Patent is remarkably effective for epitaxially growing a large diamond single crystal, formation of particles (hereinafter referred to as abnormally grown particles) losing epitaxial relation between the same and the substrates is not completely suppressed. This method has such a possibility that abnormally grown particles are generated in boundaries between the substrates. As shown in Fig. 1, an abnormally grown particle 2 is generated in a boundary region between two substrates 1 and 1' in a probability higher than those in other regions. Therefore, reduction of such a probability is an important subject in consideration of deposition of larger single-crystalline diamond.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a diamond synthesizing method having a lower probability of generation of a crystal defect by improving the method described in the above U. S. Patent.

Another object of the present invention is to provide novel diamond which is prepared by the as-improved method.

An aspect of the present invention is directed to a method of epitaxially growing diamond on a surface which is formed by a plurality of single-crystalline diamond plates from a vapor phase containing at least carbon and hydrogen. According to this method, idiomorphic single-crystalline diamond having a surface consisting substantially of a {100} plane is prepared. This single-crystalline diamond is cut substantially in parallel with the {100} plane, to obtain a plurality of diamond plates having principal surfaces consisting substantially of {100} planes and side surfaces consisting substantially of idiomorphic crystal planes. Then, the side surfaces consisting substantially of idiomorphic crystal planes are brought into contact with each other to arrange the plurality of diamond plates so that the respective principal surfaces are substantially flush with each other. Thus, a larger surface for crystal growth is formed by the principal surfaces of the diamond plates. Diamond is epitaxially grown on the larger surface from a vapor phase.

One of important features of the present invention resides in that an idiomorphic crystal is employed. In general, a crystal which is enclosed with six {100} planes and eight {111} planes is available as an idiomorphic diamond crystal. According to the present invention, such an available crystal is cut substantially in parallel with the {100} planes, to prepare a plurality of diamond plates. It is possible to obtain diamond plates having regular crystal plane orientations by cutting an idiomorphic crystal. When the as-obtained diamond plates are brought into contact with each other along idiomorphic side surfaces, it is possible to extremely suppress deviation in crystal orientation between the diamond plates.

According to the preferred aspect of the present invention, a plurality of single-crystalline diamond plates having principal surfaces consisting substantially of {100} plane or a plane which forms an angle of not more than 10° with the {100} plane are prepared. The plurality of single-crystalline diamond plates are so arranged that the respective principal surfaces are substantially flush with each other. In this step, the plurality of single-crystalline diamond plates are so fixed that an angle formed by crystal orientations in relation to the principal surfaces is not more than 5° between adjacent plates, a clearance between the adjacent plates is not more than 30 μm and difference in height in relation to the principal surfaces is not more than 30 μm between the adjacent plates. Thus obtained is a larger surface for crystal growth, which is formed by a plurality of principal surfaces. Diamond is epitaxially grown on the larger surface from a vapor phase. In such a vapor deposition step, diamond is epitaxially grown from a vapor phase having proportions A, B and C, which are obtained from the following equations I, II and III, satisfying the following conditions:

$0.5 \leq A \leq 2.0$

$0.3 \leq B \leq 2.0$

$C \leq 1.0$

$$A = ([C]/[H]) \times 100\ \% \qquad \mathrm{I}$$

$$B = ([C] - [O]/[H]) \times 100\ \% \qquad \mathrm{II}$$

C = ([O]/[H]) x 100 %   III

where [C], [O] and [H] represent molar numbers of carbon, oxygen and hydrogen atoms respectively.

According to this preferred aspect, an improved feature resides in that a plurality of single-crystalline diamond plates are so arranged and fixed that difference in height in relation to the principal surfaces is not more than 30 μm between adjacent plates. While no importance of such difference in height was recognized in the U. S. Patent, the inventors have found that the difference in height between the substrates is as important as the clearances therebetween, as the result of deep study.

In an initial stage of epitaxial growth, abnormal growth tends to occur rather in side surfaces of a diamond substrate than its principal surface. It has been conceived that this is because there is a high possibility that optimum growth conditions are brought on the principal surface while those out of the optimum conditions are brought on side surfaces. When diamond plates deviate in height from each other, therefore, there is a high possibility that a non-epitaxially grown particle 4 is formed from an exposed side surface 3 as shown in Fig. 2. When diamond plates are regularized in height, on the other hand, it is possible to suppress non-epitaxial growth which is caused by regions having different growth conditions exposed in a vapor phase. Thus, it is possible to reduce a probability of abnormal growth generated in a boundary region between diamond plates.

In order to maintain flush arrangement, the plurality of diamond plates are fixed. To this end, a plate having a flat surface is prepared and the plurality of single-crystalline diamond plates are so arranged on this plate that the principal surfaces thereof are in contact with the surface of this plate. Then, the same material is deposited on the as-arranged plurality of diamond plates, to bond the diamond plates with each other. When the as-bonded diamond plates are separated from the flat plate, it is possible to obtain a surface for crystal growth, which is formed by the principal surfaces having been in contact with the plate. Thus, it is possible to obtain a flat surface for crystal growth by arranging and fixing diamond plates on and to the flat plate. At this time, the surface roughness of the plate for receiving the diamond plates can be rendered not more than 0.1 in Rmax, while the principal surfaces of the diamond plates are preferably not more than 0.5 in Rmax. Diamond can be preferably employed as a material for bonding the plurality of diamond plates with each other. It is optimum to deposit diamond in order to eliminate difference between a jointing material and the diamond plates as to properties such as thermal expansion coefficients. The diamond is deposited on the overall plates as arranged by vapor deposition. Consequently, the plurality of plates are joined with each other by the as-deposited diamond. After the diamond plates are joined with each other, the principal surfaces thereof may be polished, so that the principal surfaces can be further flush with each other to obtain a flatter surface for crystal growth.

Another aspect of the present invention is directed to a novel diamond single crystal which is produced by the aforementioned method. This diamond single crystal has a maximum diameter of at least 15 mm and transmittance of at least 20 % as to ultraviolet light of 250 nm in wavelength. The diamond single crystal is characterized in that an angular half-width of an X-ray rocking curve in a (400) plane is not more than 100 seconds, or that a half-width of scattered light is not more than 2 cm^{-1} at a shift value 1332 cm^{-1} from excited light in a Raman scattering spectrum.

Throughout the specification, Miller indices are indicated along convention. A specific crystal plane is expressed in (hkl). While there are some planes which are equivalent to that expressed in (hkl) depending on symmetry of a crystal, such planes are expressed in {hkl} in summary. Further, a specific crystal orientation is expressed in [hkl], and orientations equivalent thereto are expressed in ⟨hkl⟩ in summary.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a model diagram for illustrating abnormal growth which tends to occur in a boundary region between diamond plates;

Fig. 2 typically shows diamond plates which are not flush wish each other;

Fig. 3 is a perspective view for illustrating a method of measuring dispersion of (100) planes in a normal direction through X-ray diffraction as to an array of a plurality of diamond plates;

Fig. 4 is a sectional view for illustrating dispersion in a normal direction with respect to (100) planes of diamond plates;

Fig. 5 is a plan view for illustrating arrangement of diamond plates;

Fig. 6A is a sectional view showing diamond plates which are arranged on a flat plate, Fig. 6B is a sectional view showing a prescribed material deposited on the diamond plates for joining the plurality of diamond plates as arranged, and Fig. 6C is a sectional view showing the as-joined diamond plates separated from the flat plate;

Fig. 7A is a perspective view showing a {100} type diamond plate;

Fig. 7B is a perspective view showing {100} type diamond plates, which are so arranged that side surfaces thereof are in contact with each other;

Fig. 8A is a perspective view showing an exemplary idiomorphic diamond crystal, Fig. 8B is a perspective view showing a diamond plate which is obtained by cutting the crystal shown in Fig. 8A, and Fig. 8C is a perspective view showing arrangement of a plurality of diamond plates which are obtained by cutting the crystal shown in Fig. 8A;

Fig. 9A is a perspective view showing another exemplary idiomorphic diamond crystal, Fig. 9B is a perspective view showing a diamond plate which is obtained by cutting the crystal shown in Fig. 9A, and Fig. 9C is a perspective view showing arrangement of a plurality of diamond plates which are obtained by cutting the crystal shown in Fig. 9A;

Fig. 10 is a perspective view showing two diamond plates which are arranged for vapor deposition;

Fig. 11 is a perspective view showing nine diamond plates which are arranged for vapor deposition;

Figs. 12A to 12D are sectional views showing steps of epitaxially growing large diamond on diamond plates which are joined with each other, illustrating the diamond plates which are arranged on a substrate, those which are joined with each other, those which are separated from the substrate, and diamond which is epitaxially grown on the as-joined diamond plates respectively;

Fig. 13 is a sectional view showing alternately deposited states of doped and undoped diamond layers;

Fig. 14 is a sectional view showing arrangement of 25 diamond plates;

Figs. 15A to 15C show an exemplary process for producing large diamond using diamond plates which are obtained by cutting an idiomorphic crystal, and Fig. 15A is a perspective view showing an idiomorphic crystal, Fig. 15B is a plan view showing a diamond plate obtained by cutting the crystal, and Fig. 15C is a perspective view showing two diamond plates which are brought into contact with each other along idiomorphic planes;

Figs. 16A to 16D are perspective views showing another exemplary process for producing large diamond using diamond plates which are obtained by cutting an idiomorphic crystal, illustrating an idiomorphic crystal, a diamond plate obtained by cutting the crystal, two diamond plates which are brought into contact with each other along idiomorphic planes, and diamond obtained by vapor deposition respectively; and

Figs. 17A to 17C are perspective views showing still another exemplary process for producing large diamond using diamond plates which are obtained by cutting an idiomorphic crystal, illustrating an idiomorphic crystal, a diamond plate obtained by cutting the crystal, and a substrate which is formed by nine diamond plates respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, it is possible to deposit diamond from a vapor phase by thermal filament CVD, plasma CVD, a plasma jet method, a combustion flame method or laser CVD. A raw material gas is preferably prepared from a gas of hydrocarbon diluted with hydrogen, such as methane. Further, a compound containing oxygen atoms such as water, carbon monoxide, carbon dioxide or hydrogen peroxide may be added to the raw material gas. In addition, an inert gas such as argon, helium or neon may be added to the raw material gas. When the raw material gas contains no oxygen, the proportion A obtained in the above equation I is within a range of 0.5 to 2.0. If the proportion A is smaller than 0.5, growth of diamond is unpractically retarded. If the proportion A exceeds 2.0, on the other hand, it is difficult to obtain diamond having excellent crystallinity on an array of a plurality of diamond plates. When the raw material gas contains oxygen atoms, the proportion B obtained in the above equation II is within a range of 0.3 to 2.0. Further, the proportion C obtained in the equation III is not more than 1.0. If the proportion B is smaller than 0.3, growth of diamond is unpractically regarded. If the proportion B exceeds 2.0, on the other hand, it is difficult to obtain diamond having excellent crystallinity on an array of a plurality of diamond plates. Also when the proportion C exceeds 1.0, it is difficult to obtain diamond having excellent crystallinity. When the raw material gas contains impurity components other than carbon, hydrogen, oxygen, fluorine and an inert element, particularly nitrogen (N), this easily leads to non-epitaxial growth. Therefore, concentration of the impurity components with respect to overall elements contained in the gas is preferably not more than 500 p.p.m., excepting a dopant which may be positively employed for bringing vapor-deposited diamond into a

semiconductor state.

For the purpose of vapor deposition, single-crystalline diamond plates can be maintained preferably at temperatures of about 1000 to 1400 °C, more preferably about 1050 to 1250 °C. Due to vapor deposition in such a high temperature range, it is possible to effectively suppress formation of polycrystalline diamond.

The diamond plates for epitaxial growth are preferably regular in quality. Therefore, artificial diamond single crystals which are synthesized under high pressures are preferably employed for the diamond plates. Alternatively, the diamond plates may be prepared from natural single-crystalline diamond or diamond which is epitaxially grown by vapor deposition.

The principal surface of each diamond plate consists essentially of a {100} plane or a plane which forms an angle of not more than 10°, preferably not more than 3°, with the {100} plane. The principal surfaces are preferably so polished that surface roughness thereof is not more than 0.5 in Rmax. Edges and corners of the diamond plates are effectively chamfered with widths of not more than 20 µm, to be protected against chipping. The diamond plates are provided in shapes which are suitable for filling up a plane of a square, a rectangle, a triangle or a hexagon. A required number of such diamond plates are tightly arranged and fixed to each other.

In arrangement of the diamond plates, it is possible to confirm whether or not an angle formed by crystal orientations of adjacent plates is within 5°, preferably within 3°, through X-ray diffraction or electron beam diffraction by a method shown in Fig. 3, for example. Referring to Fig. 3, positions of an X-ray generator 11 and an X-ray detector 12 are fixed while a sample holder 15 is so translated or swingingly rotated that a (400) diffracted beam 14 of an X-ray 16 enters the X-ray detector 12. ⟨100⟩ directions of the substrates coincide with a direction of a straight line MN appearing in Fig. 3. Symbol M denotes a point of incidence of the X-ray 16 upon a (100) plane, and symbol θ_1 denotes an angle which is formed by the X-ray 16, the (400) diffracted beam 14 and the (100) plane. Symbols H_1 and H_2 denote points on the X-ray 16 and the (400) diffracted beam 14, which are equally separated from the point M of incidence. Symbol N denotes an intersection between perpendicular lines drawn from the points H_1 and H_2 on a plane which is defined by the X-ray 16 and the diffracted beam 14. Since the X-ray generator 11 and the X-ray detector 12 are fixed, it is possible to detect dispersion in the ⟨100⟩ orientations of the substrates by measuring the swingingly rotational angle of the sample holder 15. Accuracy of this measuring method is about 0.1.

When a plurality of substrates are arranged, an angle formed by crystal orientations of adjacent substrates is not more than 5 °C, and a clearance between the adjacent substrates is not more than 30 µm, more preferably not more than 15 µm. Referring to Fig. 4, a boundary is observed in an integrated portion of adjacent growth layers 21 and 21' when an angle α formed by crystal orientations of adjacent substrates 20 and 20', i.e., normal directions of crystal planes, is within 5°, while no such grain boundary is observed in upper portions of the growth layers 21 and 21'. Substantially homogeneous single-crystalline diamond layers are grown in such upper portions. If the angle α is in excess of 5°, however, a grain boundary tends to remain, leading to occurrence of a defect. Referring to Fig. 5, on the other hand, an angle β which is formed by crystal orientations parallel to principal surfaces of adjacent substrates 25 and 25' is preferably not more than 5° either. If the angle β is in excess of 5°, a crystal defect is easily caused in a boundary between the substrates 25 and 25'. A clearance δ between the substrates 25 and 25' is not more than 30 µm, and more preferably not more than 15 µm. If the clearance δ exceeds 30 µm, a crystal defect easily takes place in the boundary between the substrates 25 and 25' when large-area diamond is to be grown.

According to this method, it is possible to confirm that the angle α is not more than 5°, preferably not more than 3° by the aforementioned measuring method. Referring to Fig. 6A, it is possible to arrange diamond plates 30 having pairs of parallel principal surfaces on a flat substrate 31 and to perform the aforementioned measurement on single principal surfaces. If deviation exceeding 5° is recognized, the corresponding one of the plates 30 is rotated in a direction for reducing the deviation or replaced by another plate until the deviation is not more than 5°. When the deviation is suppressed to not more than 5°, more preferably not more than 3°, a binder is deposited as shown in Fig. 6B, to join the diamond plates 30 with each other. As hereinabove described, a diamond layer 32 is preferably deposited from a vapor phase. Then, the as-joined diamond plates 30' are separated from the substrate 31, so that it is possible to obtain a surface 30'a for epitaxial growth, which is formed by the other principal surfaces having been in contact with the substrate 31 (Fig. 6C). Alternatively, it is possible to reduce deviation exceeding 5° by polishing principal surfaces having been in contact with the flat substrate 31 after the plurality of diamond plates are joined with each other. In this case, the aforementioned measurement may be performed after the principal surfaces of the joined diamond plates are polished. Thus, a flatter surface for epitaxial growth is prepared.

According to the present invention, difference in height between principal surfaces of the diamond plates is not more than 30 µm, more preferably not more than 10 µm. If the difference is in excess of 30

μm, a probability of occurrence of abnormal growth is increased as described above. The diamond plates are arranged on a flat substrate and joined with each other as hereinabove described, so that the principal surfaces are flush with each other. The substrate for receiving the diamond plates is not more than 0.1 in Rmax as to surface roughness, for example. The principal surfaces of the diamond plates are not more than 0.5 in Rmax as to surface roughness either, for example. The principal surfaces which are arranged on a flat substrate can be flush with each other. Then, the diamond plates are fixed. For the fixation, it is possible to deposit diamond on the diamond plates from a vapor phase, as hereinabove described. The diamond plates which are joined with each other are separated from the substrate, to be subjected to synthesis of diamond having a larger size. At this time, it is most effective to polish the surfaces for crystal growth, so that the same are flush with each other. Due to such polishing, a flatter surface for crystal growth is obtained. The difference in height between the principal surfaces of the diamond plates is measured by an atomic force microscope, for example.

In epitaxial growth on a {100} plane at a temperature of about 1000 to 1400 °C, it is possible to more effectively suppress generation of twin crystals and secondary nuclei than epitaxial growth on another crystal plane. For a reason similar to this, side surfaces of the diamond plates preferably consist essentially of {100} planes, so that no crystals of abnormal orientations are generated from the side surfaces toward the principal surfaces. When the principal surface of each diamond plate is formed by a {100} plane, side surfaces enclosing the principal surface can be prepared from {100} planes which are perpendicular to the principal surface (see Fig. 7A). In this case, it is possible to arrange a plurality of diamond plates so that the side surfaces of {100} planes are in contact with each other (see Fig. 7B).

The plurality of diamond plates are preferably prepared from an idiomorphic single crystal. The term "idiomorphic diamond crystal" indicates a crystal of diamond which is freely grown with no hindrance by external conditions into a crystalline form completely enclosed by specific crystal planes dominated by symmetry of its crystal structure. Such an idiomorphic diamond crystal can be prepared from either natural diamond or artificial diamond synthesized under high pressure. In general, an idiomorphic diamond crystal can take a polyhedral structure (called a hexa-oxtahedron) consisting of six (100) planes and eight (111) planes as shown in Fig. 8A or 9A, for example. When a crystal 41 shown in Fig. 8A is employed, it is possible to prepare a diamond plate 42 in a shape shown in Fig. 8B by cutting the crystal 41 substantially in parallel with a (100) plane 41a. In this diamond plate 42, a principal surface consists essentially of a (100) plane, while four side surfaces enclosing the principal surface consists essentially of idiomorphic (111) crystal planes. When such cutting is further performed, it is possible to prepare a plurality of diamond plates having principal surfaces of (100) planes and side surfaces of idiomorphic crystal planes. Then, one of two such diamond plates 42 and 42' is inverted as shown in Fig. 8C, for example, so that the diamond plates 42 and 42' are in contact with each other along single idiomorphic crystal planes thereof. The two diamond plates 42 and 42' are bonded to each other in the aforementioned manner. Thus, a wider substrate 43 is obtained so that a surface for crystal growth is formed by a (100) plane. When a crystal 51 shown in Fig. 9A is employed, on the other hand, a plurality of diamond plates are obtained by cutting the crystal 51 substantially in parallel with (100) planes similarly to the above. Fig. 9B shows one of the as-obtained diamond plates 52. In this diamond plate 52, a principal surface 52a consists essentially of a (100) plane, while four principal side surfaces 52b enclosing the principal surface 52a also consist essentially of idiomorphic (100) planes. Other diamond plates 52 obtained by cutting the crystal 51 also have side surfaces of (100) planes. Then, the diamond plates 52 are brought into contact with each other along the idiomorphic side surfaces and fixed to each other, thereby obtaining a wider substrate 53.

In an idiomorphic diamond crystal, deviation in crystal plane orientation is hardly observed although a small amount of microdefects are present. Therefore, it is possible to prepare diamond plates having regular crystal plane orientations by cutting an idiomorphic crystal, as hereinabove described. Further, it is possible to extremely suppress deviation in crystal orientation between such diamond plates by bringing the diamond plates into contact with each other along idiomorphic side surfaces. Such contact along the idiomorphic side surfaces is effective for suppressing deviation in crystal orientation in a surface for epitaxial growth.

According to the present invention, a substrate surface for crystal growth can be etched in a depth of at least 1 nm, more preferably at least 10 nm, in advance of deposition of diamond. The substrate surface can be etched by plasma which is mainly composed of hydrogen. A gas for forming such plasma is prepared from a mixed gas containing 99 % of hydrogen and 1 % of oxygen, for example. The etching step can be carried out in a microwave plasma CVD apparatus for synthesizing diamond, to remove flaws and dust from the substrate surface for forming a clean surface.

According to the present invention, further, it is possible to deposit diamond while doping the same with a dopant such as boron, nitrogen or phosphorus. Such a dopant is adapted to control electrical or optical

properties of the diamond. After doped semiconductor diamond is deposited on the substrate, it is possible to deposit undoped insulator diamond thereon. When electric discharge machining is carried out along the doped diamond layer in this case, it is possible to selectively extract the undoped diamond. When deposition with doping and that with no doping is repeated, it is possible to obtain a plurality of undoped diamond films having prescribed thicknesses by electric discharge machining.

According to the aforementioned process, it is possible to form large single-crystalline diamond of high quality on a substrate which is formed by an array of a plurality of diamond plates. There still remains a possibility that grain boundaries having small inclinations are present in the as-obtained crystal due to slight deviation in crystal orientation between the diamond plates. When processing for reducing the probability of abnormal growth is carried out as hereinabove described, however, it is possible to suppress scattering of light and occurrence of a large amount of defects caused by such grain boundaries. According to the inventive process, novel vapor-deposited diamond having the following features is obtained:

(i) The maximum diameter is at least 15 nm.

(ii) Transmittance for ultraviolet light of 250 nm in wavelength is at least 20 %.

(iii) An angular half-width of an X-ray rocking curve in a (400) plane is not more than 100 seconds, or a half-width of a peak at 1332 cm^{-1} in a Raman scattering spectrum is not more than 2 cm^{-1}.

Example 1

Study of Growth Temperature and Growth Plane

Conditions as to a growth temperature and a growth plane were studied as follows:

Diamond single crystals for forming substrates were prepared by slicing a natural type IIa diamond crystal and polishing the same. Six, six and six substrates were prepared to have principal surfaces of {111}, {100} and {110} orientations were prepared respectively. In each of the {100} substrates, every side surface was at an angle of within 3° from the {100} plane. All substrates were 4 mm by 4 mm in size and 2.0 mm in thickness. It was confirmed by X-ray diffraction that every substrate had deviation of not more than 2° in plane orientation from each index plane. All edges of these substrates were chamfered to expose the {100} planes in widths of 50 to 200 μm. Two substrates were employed for each type of principal surface to carry out vapor deposition at three types of substrate temperatures of 850°C, 1150°C and 1450°C respectively. In every case, microwave plasma CVD was employed with a gas containing 89.5 % of hydrogen (H_2) and 1.5 % of methane (CH_4) and a total gas flow rate of 300 sccm. Only nitrogen was detected as an impurity contained in such a raw material gas, at a rate of 5 to 20 p.p.m. with respect to the overall gas. Diamond was intermittently grown four times, with growth times of 50 hours each, i.e., 200 hours in total. The surface of each substrate was cleaned with hydrogen plasma for 3 hours in advance of the first growth. Table 1 shows thicknesses of the as-grown films.

Table 1

Plane/Temperature	850°C	1150°C	1450°C
{111}	400μm	490μm	20μm
{100}	220μm	210μm	10μm
{110}	650μm	720μm	80μm

Then, growth end surfaces were polished and full widths at half maximums of diamond signals (1332 cm^{-1}) were obtained by high resolution Raman spectrometry. Table 2 shows the results. As to the {111} and {110} substrates, the results at the substrate temperatures of 1450°C were regarded substantially as being measured values in relation to the substrates since epitaxial layers of about 10 to 20 μm were lost in polishing. As to the epitaxial films, therefore, the film epitaxially grown on the {100} substrate at 1150°C exhibited the sharpest peak and conceived as having the most excellent crystallinity.

Table 2

Plane/Temperature	850 °C	1150 °C	1450 °C
{111}	4.6	4.9	(1.6)
{100}	2.2	1.8	(1.7)
{110}	3.7	3.5	3.0

As to the samples grown at 850 ° and 1150 °C respectively, further, upper portions of 200 μm of the epitaxial layers were extracted. These portions were extracted by slicing as to the {100} and {110} substrates, and by etching from the substrates with laser beams converged from the substrate sides as to the {111} substrates. Substrate-side surfaces of the as-extracted portions were respectively polished to obtain six double-polished diamond films of 180 μm in thickness. It was impossible to carry out such processing on the samples grown at 1450 °C, due to insufficient thicknesses of the epitaxially grown films. In visual observation, it seemed that transparent diamond was attained entirely over two {110} epitaxial films and the {100} epitaxial films grown at 1150 °C, while black spots were partially observed on the remaining substrates. Further, numbers of cracks were observed on the {110} and {111} epitaxial films. Table 3 shows linear transmittance values for visible light of 250 nm in wavelength. The epitaxial film which was grown on the {100} substrate at 1150 °C exhibited the maximum value.

Table 3

Plane/Temperature	850 °C	1150 °C	1450 °C
{111}	35 %	35 %	-
{100}	50 %	65 %	-
{110}	40 %	50 %	-

Three type Ib diamond single-crystalline {100} substrates of 1 cm by 1 cm by 2 mm were prepared by artificial high-pressure synthesis. It was confirmed by reflective electron diffraction that a deviation angle of each surface for growth was within 0.5 ° from the {100} plane. Side surfaces of the substrates were at angles of within 3 ° from the {100} planes. As to each of two samples among the three diamond substrates, diamond doped with 1000 p.p.m. of boron (B) was epitaxially grown on a single side by microwave plasma CVD in a thickness of 2 μm. As to all three substrates, on the other hand, transverse holes of 0.3 mm in diameter and 1 mm in depth were formed on the side surfaces with point-converged laser beams, and alumel-chromel thermocouples were inserted in these holes to measure temperatures in film formation. Films were epitaxially grown on the three substrates by thermal filament CVD, with filaments of tantalum (Ta) of 0.2 mm in diameter. Six filaments were provided at intervals of 3 mm on each sample, at a filament temperature of 1980 °C and distances of 6 mm between the filaments and the substrate upper surface. 99 % of hydrogen and 1 % of methane were introduced into an apparatus under 70 Torr to heat the filaments, whereby the substrate temperatures reached constant levels of 950 °C after 30 minutes. The substrate having a film doped with B was energized and heated to 1050 °C or 1150 °C. The films were formed for 70 hours in these states, and thereafter the surfaces were observed. Samples having higher substrate temperatures exhibited smaller numbers of abnormal depth.

Study of Substrate Surface Height

Two {100} single-crystalline diamond plates of 6.0 mm by 4.0 mm by 300 ± 25 μm in size were prepared by working and polishing type Ib high-pressure synthesized diamond. The two diamond plates were arranged as shown in Fig. 10, so that diamond was grown thereon by microwave plasma CVD. A raw material gas was prepared from a mixed gas containing 98 % of hydrogen and 2 % of methane (proportion A = 1.0). At this time, diamond was grown under conditions of a pressure of 100 Torr and a plate temperature of 900 °C. In such a system, the space between the two plates and difference in height between the plate surfaces were varied to carry out experiments. A deviation angle between crystal planes of the two plates was not more than about 3 °. Table 4 shows the results.

Table 4

Experiment No.	Deviation Angle (°)	Space (μm)	Difference in Height (μm)	State of Crystal as Obtained
1	1.0	10	20	X
2	2.5	25	10	X
3	0.5	40	10	Y
4	1.0	10	35	Z
5	1.0	35	40	Z

X: no polycrystal in the boundary between the plates
Y: slight polycrystal in the boundary
Z: some polycrystals in the boundary

Production of Large Diamond

18 {100} single-crystalline diamond plates of 4.0 mm by 4.0 mm by 300 ± 20 μm in size were prepared by working and polishing type Ib high-pressure synthesized diamond. Then, a pair of 3 by 3 arrays of nine diamond plates as shown in Fig. 11 were prepared. In each array, diamond plates 60 were arranged on a flat substrate 61 of Si, as shown in Fig. 12A. Then, a diamond layer 62 was deposited from a vapor phase in a thickness of about 100 μm, as shown in Fig. 12B. Thus, the nine diamond plates were bonded with each other in each array. The diamond layer 62 was deposited by microwave plasma CVD with a mixed gas containing 3 % of methane and 97 % of hydrogen under conditions of a pressure of 100 Torr and a plate temperature of 950°C. Then, the as-bonded diamond plates 60 were separated from the substrate 61 as shown in Fig. 12C, to grow a large diamond plate 63 on surfaces 60a which had been in contact with the substrate 61. In one of the as-obtained two large diamond plates 63, the surfaces 60a having been in contact with the substrate 61 were mechanically polished. Then, back surfaces were mechanically polished and the large diamond plate 63 was thereafter treated with chromic acid. The other large diamond plate 63 was subjected to vapor-phase growth as such, through no polishing step. In the polished sample, steps between adjacent ones of the diamond plates 60 were not more than 0.1 μm. In the unpolished sample, on the other hand, steps of 40 μm at the maximum were recognized. In each sample, a clearance between adjacent diamond plates 60 was not more than 20 μm, and a deviation angle of crystal orientations was not more than 3.0°. Referring to Fig. 12D, diamond 64 was epitaxially grown on the large diamond plate 63 along a plasma jet method in a thickness of 1000 μm. A gas as introduced consisted of 1 slm of argon, 2 slm of hydrogen, 20 sccm of methane and 6 sccm of carbon dioxide. This diamond plate 63 was maintained at a temperature of 1050°C. A growth end surface was mirror-polished, whereafter the diamond plate 63 was removed by polishing, to separate the vapor-deposited diamond 64. Transparent diamond was obtained on those of the plates 60 which were polished to be flush with each other, with transmittance of at least 68 % with respect to light of 350 nm as a whole. It was possible to regard this diamond substantially as a large single crystal of high quality. When diamond was deposited on the unpolished plate, on the other hand, black spots resulting from abnormal growth were recognized in boundaries between the diamond plates 60. In the as-obtained diamond, transmittance for light of 350 nm was not more than 5 % in the lowest part. Thus, it has been clarified that levelling by polishing is important in order to produce large diamond.

Example 2

Nine {100} single-crystalline diamond plates of 4.0 mm by 4.0 mm by 300 ± 20 μm in size were prepared by working and polishing type Ib high-pressure synthesized diamond. These plates were arranged and bonded with each other similarly to Example 1, to prepare a substrate surface having no steps by polishing. Semiconductor single-crystalline diamond doped with boron was deposited on the as-prepared substrate surface in a thickness of 300 μm, whereafter an undoped insulator diamond single crystal was grown thereon in a thickness of 700 μm. Such a series of process was repeated three times, to form a multilayer structure shown in Fig. 13. Referring to Fig. 13, doped diamond layers 71 and undoped diamond

layers 72 are alternately deposited on a substrate 70. In the series of process, diamond was grown by microwave plasma CVD. A raw material gas was prepared from a mixed gas of methane and hydrogen. Concentration of methane was 2 %, and a proportion A was 1.0. For the purpose of doping, 250 p.p.m. of diborane with respect to methane was added to the raw material gas. The substrate temperature was maintained at 1000 °C. After the growth, portions of diamond horizontally projecting from the substrate 70 were removed by laser beam machining. The multilayer structure was cut along the layers 71 doped with B by electric discharge machining. After polishing of the as-cut surfaces, it was possible to obtain three transparent undoped diamond crystals of 12 mm by 12 mm by 700 µm. These three diamond crystals entirely exhibited transmittance values of at least 65 % with respect to light of 350 nm. The substrate 70 separated from the as-deposited diamond was re-usable for producing large diamond.

Example 3

As shown in Fig. 14, 25 {100} single-crystalline diamond plates of 4.0 mm by 4.0 mm by 300 ± 20 µm in size were arranged on a flat plate of Si in the form of a 5 by 5 array. Clearances between the diamond plates were suppressed within 15 µm. Diamond was grown on such an array of diamond plates by microwave plasma CVD. A raw material gas was prepared from a hydrogen-methane mixed gas having methane concentration of 3 % (proportion A = 1.5). The microwave plasma CVD was carried out under conditions of a pressure of 100 Torr and a substrate temperature of 950 °C for 100 hours. The diamond was deposited on the diamond plates in a thickness of 200 µm, whereby the 25 diamond plates were joined with each other to provide a large substrate. Both principal surfaces of the large substrate were mechanically polished, whereafter the substrate was washed with dichromic acid. Deviation angles in crystal plane orientations between the 25 diamond plates forming the large substrate examined by X-ray diffraction were 1.5° at the maximum. Further, steps between the diamond plates were 0.1 µm at the maximum. Then, a semiconductor diamond single crystal doped with boron was grown on a surface of the large substrate opposite to that provided with the joined diamond layers. A raw material gas was prepared from a hydrogen-methane mixed gas having methane concentration of 2 % (proportion A = 1.0), with addition of 10 p.p.m. of diborane. The substrate temperature was maintained at 1000 °C, to grow the diamond doped with boron to a thickness of 300 µm under a pressure of 120 Torr for 150 hours. Then, undoped diamond was epitaxially grown with a raw material gas containing hydrogen mixed with 2 % of methane and 0.3 % of H_2O (proportion B = 0.85, proportion C = 0.15). The undoped diamond of high purity was grown to a thickness of 700 µm under conditions of a pressure of 120 Torr and a substrate temperature of 1100 °C. The process of depositing a doped layer and a high-purity undoped layer was repeated three times. The as-deposited diamond was cut along the doped layers by electric discharge machining, to obtain three high-purity diamond single crystals. Both surfaces of these single crystals were mirror-polished and thereafter outer edge portions of inferior quality were removed by laser beam machining, to obtain colorless transparent diamond single crystals which were about 20 mm square and 500 to 600 µm in thickness. The as-obtained diamond single crystals had maximum diameters of about 27 mm. Optical transmittance values of these crystals were measured in relation to visible and ultraviolet regions, to find that ultraviolet absorption edges were 225 nm along the overall surfaces, and transmittance values at 250 nm were 45 % at the minimum. Three pairs were selected from the as-obtained three crystals, and subjected to measurement of double crystal X-ray rocking curves of (400) planes with X-rays of CuKα1. Half-widths of the rocking curves were 43 seconds, 40 seconds and 41 seconds respectively. A half-width of a Raman scattering spectrum shifting to and appearing at a position of 1332 cm^{-1} from excited light which was emitted from an argon ion laser of 514.5 nm in wavelength was 1.7 cm^{-1} upon measurement with a spectroscope of 0.7 cm^{-1} in resolution.

Characteristics of two type IIa natural diamond single crystals, three type Ia natural diamond single crystals, four type Ib high-pressure synthetic diamond single crystals and two type IIa high-pressure synthesized diamond single crystals were examined in comparison with the aforementioned three diamond single crystals. Table 5 shows the results. In such comparison, light transmittance values were measured by mirror-polishing light incident/outgoing surfaces. In measurement of double crystal X-ray rocking curves, the same high-pressure synthesized type Ib diamond single crystals were employed as primary crystals. It was proved from the results of the measurement that the inventive diamond is large diamond of high quality, which has been impossible to attain. Terms appearing in Table 5 indicate the following values:

Diameter: maximum diametral length (mm)
Thickness: optical path length (mm) of diamond in measurement of light transmittance
Absorption Edge: transmittance threshold wavelength (nm) in visible region to ultraviolet region
Transmittance: transmittance at 250 nm (72 % at the maximum due to refractive index of diamond)

X-Ray Half-Width: angular half-width (sec.) of X-ray rocking curve measured in the above method

Raman Half-Width: half-width (sec.) of scattering peak around 1332 cm^{-1} measured in the aforementioned method

Table 5

Comparison of Characteristics of Various Diamond Single Crystal								
	Sample	Type	Diameter (mm)	Thickness (mm)	Absorption Edge(mm)	Transmittance (%)	X-Ray Half-Width (sec.)	Raman Half-Width (sec.)
Example	1	Vapor Deposition	27	0.6	225	47	36	1.7
	2	Vapor Deposition	27	0.6	225	47	35	1.7
	3	Vapor Deposition	27	0.6	225	45	35	1.7
Comparative Example	4	Natural IIa	4	0.5	225	43	600	2.2
	5	Natural IIa	4	0.5	225	45	750	
	6	Natural Ia	3	2.0	305	0	64	2.4
	7	Natural Ia	3	2.0	310	0	8	
	8	Natural Ia	3	2.5	305	0	10	
	9	High-Pressure Synthesis Ib	4	0.4	420	0	6	1.9
	10	High-Pressure Synthesis Ib	4	0.4	410	0	8	2.0
	11	High-Pressure Synthesis Ib	4	0.4	420	0	6	2.0
	12	High-Pressure Synthesis IIa	3	0.3	225	55	6	1.7
	13	High-Pressure Synthesis IIa	3	0.3	225	56	6	1.9

Example 4

A hexa-octahedral diamond crystal 74 was prepared by high-pressure synthesis as shown in Fig. 15A, and sliced in parallel with a square plane appearing in the crystal, to obtain a plate 75 in a shape shown in Fig. 15B. A plane orientation of a major surface of this plate 75 exhibited deviation of within 0.05° from a {100} plane. Four such plates were obtained by similar slicing. Both surfaces of the plates were mirror-polished, and two of the four plates were inverted and brought into contact with the remaining non-inverted plates, to form two pairs of such plates 75 and 75' as shown in Fig. 15C. Diamond was grown by microwave plasma CVD.

In such growth of diamond, one of the two pairs of plates 75 and 75' was subjected to etching of a surface layer by 1 µm by plasma of a mixed gas containing 99 % of hydrogen and 1 % of oxygen in a microwave plasma CVD apparatus for 10 hours. Following this etching, the diamond was grown under the following conditions:

Methane:	3 %
Hydrogen:	71 %
Oxygen:	1 %
Argon:	25 %
Substrate Temperature:	900°C
Growth Time:	100 hours

The other pair was subjected to growth of diamond through no etching process. Consequently, diamond of 80 µm was grown to provide integral diamond of two diamond crystals in each case. Deviation in orientation of the diamond forming the substrate was within 0.05° in each case. However, while concentration of abnormal growth recognized on the surface was 0.5/mm^2 in the etched sample, while that in the unetched sample was 3/mm^2.

Example 5

A hexa-octahedral type Ib diamond single crystal 81 was prepared as shown in Fig. 16A by high-pressure synthesis. This diamond single crystal 81 was sliced in parallel with a (100) plane 81a serving as a growth surface, to obtain a diamond crystal plate 82 of 100 µm in thickness, as shown in Fig. 16B. It was confirmed by X-ray diffraction that deviation between a plane orientation of the as-cut surface of the diamond crystal plate 82 and a (100) plane was within 0.05°.

Two such diamond crystal plates 82 and 82' were prepared with mirror-polished (100) planes 81a and cut surfaces, and one of such diamond crystal plates 82 and 82' was inverted to be in contact with the other one along (111) planes as shown in Fig. 16C, thereby forming a substrate 83 for vapor deposition.

A raw material gas was supplied by well-known microwave plasma CVD so that methane, hydrogen, oxygen and argon were 3 %, 71 %, 1% and 25 % respectively, thereby growing a diamond thin film on the substrate 83 under conditions of a gas pressure of 80 Torr and a substrate temperature of 900°C for 500 hours.

After growth of the diamond, the substrate 83 was extracted to confirm that a diamond thin film of about 500 µm in thickness was integrally grown thereon.

Deviation between plane orientations of the two diamond crystal plates 82 and 82' was examined by a measuring method employing electron beam diffraction, to find that the deviation was suppressed to a level within 0.05°.

A growth surface of the integrated diamond thin film was mirror-polished and the substrate portion was removed by polishing to obtain an integral diamond single body 84 of 450 µm in thickness as shown in Fig. 16D. In visual observation, no strong reflection was recognized on a junction part of the diamond thin film which was grown on the two diamond crystal plates in particular.

A sample surface of the diamond single body 84 was polished and observed with an STM (scanning tunnel electron microscope), to confirm that neither polycrystalline components nor amorphous components were present in a junction part of the as-grown diamond layer, although grain boundaries having small inclinations were provided.

Example 6

A hexa-octahedral type Ib diamond single crystal 85 was prepared by high-pressure synthesis, as shown in Fig. 17A. The diamond single crystal 85 was sliced in parallel with a (100) plane 85a, serving as a growth surface, to obtain a diamond crystal plate 86 of 150 μm in thickness as shown in Fig. 17B. It was confirmed by X-ray diffraction that deviation between a plane orientation of the as-cut surface of the diamond crystal plate 86 and a (100) plane was within 0.1°.

Nine diamond crystal plates 86 were prepared with mirror-polished (100) planes 85a and cut surfaces, and arranged to be in contact with each other along (100) planes as shown in Fig. 17C, to form a substrate 87 for vapor deposition.

A raw material gas was supplied by well-known microwave plasma CVD so that methane, hydrogen, oxygen and argon were 5 %, 69 %, 1 % and 25 % respectively, thereby growing a diamond thin film on the substrate 87 under conditions of a gas pressure of 75 Torr and a substrate temperature of 1050°C for 500 hours.

After growth of the diamond, the substrate 87 was extracted to confirm that a diamond thin film of about 1000 μm in thickness was integrally grown on this substrate 87.

Deviation between plane orientations of the nine diamond crystal plates 86 was examined by a measuring method employing electron beam diffraction, to find that the deviation was suppressed to within 0.2° at the maximum.

A growth surface of the integrated diamond thin film was mirror-polished and the substrate portion was removed by polishing to obtain an integral diamond single body of 800 μm in thickness. In visual observation, no strong reflection was recognized on a junction part of the diamond thin film grown on the nine diamond crystal plates in particular.

A sample surface of the diamond single body was polished and observed with an STM, to confirm that neither polycrystalline components nor amorphous components were present in a junction part of the as-grown diamond layer, although grain boundaries having small inclinations were provided.

According to the present invention, a homogeneous large diamond single crystal is provided. The diamond obtained according to the present invention has characteristics suitable as a substrate for an optical or semiconductor device, in particular. According to the present invention, further, it is possible to obtain a doped diamond single crystal. The diamond single crystal according to the present invention can be widely applied to a cutting edge of a precise tool, a tool having wear resistance and heat resistance, a semiconductor base material, a substrate for heat radiation, a semiconductor material, an optical material, or an acoustic diaphragm.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

Claims

1. A method of epitaxially growing diamond on a surface being formed by a plurality of single-crystalline diamond plates from a vapor phase containing at least carbon and hydrogen, said method comprising:

a step of preparing idiomorphic single-crystalline diamond (41, 51, 74, 81, 85) having a surface consisting substantially of a {100} plane;

a step of cutting said single-crystalline diamond (41, 51, 74, 81, 85) substantially in parallel with said {100} plane, thereby obtaining a plurality of diamond plates (42, 52, 75, 82, 86) having principal surfaces consisting substantially of {100} planes and side surfaces consisting substantially of idiomorphic crystal planes;

a step of bringing said side surfaces consisting substantially of idiomorphic crystal planes into contact with each other for arranging said plurality of diamond plates (42, 52, 75, 82, 86) so that respective said principal surfaces are substantially flush with each other, thereby obtaining a larger surface for crystal growth being formed by said principal surfaces; and

a step of epitaxially growing diamond on said larger surface from said vapor phase.

2. A method in accordance with claim 1, wherein said plurality of single-crystalline diamond plates (42, 52, 75, 82, 86) are so fixed in said bringing step that an angle formed by crystal orientations in relation to said principal surfaces between adjacent said diamond plates is not more than 5°, a clearance between adjacent said diamond plates is not more than 30 μm, and difference in height in relation to said principal surfaces is not more than 30 μm between adjacent said diamond plates,

said diamond being epitaxially grown from a vapor phase having proportions A, B and C, being obtained from the following equations I, II and III respectively, satisfying the following conditions:
$0.5 \leq A \leq 2.0$
$0.3 \leq B \leq 2.0$
$C \leq 1.0$

$$A = ([C]/[H]) \times 100\ \% \qquad \text{I}$$

$$B = ([C] - [O]/[H]) \times 100\ \% \qquad \text{II}$$

$$C = ([O]/[H]) \times 100\ \% \qquad \text{III}$$

where [C], [O] and [H] represent molar numbers of carbon, oxygen and hydrogen atoms respectively.

3. A method of epitaxially growing diamond on a surface being formed by a plurality of single-crystalline diamond plates from a vapor phase containing at least carbon and hydrogen, said method comprising:
(a) a step of preparing a plurality of single-crystalline diamond plates (60) having principal surfaces consisting substantially of a {100} plane or a plane which forms an angle of not more than 10° with the {100} plane;
(b) a step of arranging said plurality of single-crystalline diamond plates (60) so that the respective principal surfaces are substantially flush with each other, thereby obtaining a larger surface for crystal growth being formed by said principal surfaces; and
(c) a step of epitaxially growing diamond (64) on said larger surface from said vapor phase,
said plurality of single-crystalline diamond plates (60) being so fixed that an angle formed by crystal orientations in relation to said principal surfaces between adjacent said diamond plates is not more than 5°, a clearance between adjacent said diamond plates is not more than 30 µm, and difference in height in relation to said principal surfaces is not more than 30 µm between adjacent said diamond plates,
said diamond being epitaxially grown from the vapor phase having proportions A, B and C, being obtained from the following equations I, II and III respectively, satisfying the following conditions:
$0.5 \leq A \leq 2.0$
$0.3 \leq B \leq 2.0$
$C \leq 1.0$

$$A = ([C]/[H]) \times 100\ \% \qquad \text{I}$$

$$B = ([C] - [O]/[H]) \times 100\ \% \qquad \text{II}$$

$$C = ([O]/[H]) \times 100\ \% \qquad \text{III}$$

where [C], [O] and [H] represent molar numbers of carbon, oxygen and hydrogen atoms respectively.

4. A method in accordance with claim 3, wherein said larger surface is maintained at a temperature within a range of about 1000 to 1400°C in said step (c).

5. A method in accordance with claim 3, wherein said step (b) further comprises a step of etching said principal surfaces of arranged said diamond plates in depths of at least 1 nm.

6. A method in accordance with claim 5, wherein said etching step is carried out with plasma being mainly composed of hydrogen.

7. A method in accordance with claim 3, wherein said principal surfaces consist substantially of a plane of which inclination with the {100} plane is not more than 3°.

8. A method in accordance with claim 3, wherein said step (b) further comprises:
a step of preparing a plate (31, 61) having a flat surface,
a step of arranging said plurality of single-crystalline diamond plates (30, 60) on said plate (31, 61) so that said principal surfaces are in contact with said surface of said plate (31, 61),

a step of depositing the same material (32, 62) on arranged said plurality of single-crystalline diamond plates (30, 60) thereby bonding the same with each other, and

a step of separating bonded said plurality of single-crystalline diamond plates (30, 60) from said plate (31, 61) thereby obtaining a surface for crystal growth being formed by said principal surfaces having been in contact with said plate.

9. A method in accordance with claim 8, wherein diamond is deposited from a vapor phase as said material (32, 62) for bonding.

10. A method in accordance with claim 8 or 9, further comprising a step of polishing said principal surfaces of bonded said single-crystalline diamond plates (30, 60) for obtaining a flatter surface for crystal growth.

11. A method in accordance with claim 3, wherein said step (b) further comprises a step of checking dispersion in crystal orientation in relation to said principal surfaces by X-ray diffraction or electron beam diffraction.

12. A method in accordance with claim 3, wherein each of said plurality of single-crystalline diamond plates has four side surfaces enclosing said principal surface and each consisting essentially of a {100} plane or a plane which forms an angle of not more than 10° with the {100} plane.

13. A method in accordance with claim 3, wherein said step (a) further comprises:

a step of preparing idiomorphic single-crystalline diamond (41, 51, 74, 81, 85) having a surface consisting substantially of a {100} plane; and

a step of cutting said single-crystalline diamond (41, 51, 74, 81, 85) substantially in parallel with said {100} plane, thereby obtaining a plurality of diamond plates (42, 52, 75, 82, 86) having principal surfaces consisting substantially of {100} planes and side surfaces consisting substantially of idiomorphic crystal planes, and

said step (b) furtehr comprises:

a step of bringing said side surfaces consisting substantially of idiomorphic crystal planes into contact with each other for arranging said plurality of diamond plates(42, 52, 75, 82, 86) so that respective said principal surfaces are substantially flush with each other.

14. A method in accordance with claim 13, wherein said idiomorphic crystal planes forming said side surfaces are {100} planes.

15. A method in accordance with claim 13, wherein said idiomorphic crystal planes forming said side surfaces are {111} planes.

16. A method in accordance with claim 3, wherein said diamond (71) is deposited with addition of an impurity in said step (c).

17. A method in accordance with claim 3, wherein said step (c) comprises a step of successively depositing doped diamond (71) and undoped diamond (72),

said undoped diamond (72) being selectively separated by working being carried out along said doped diamond (71).

18. Vapor-deposited diamond comprising the following characteristics:

(i) a maximum diameter of at least 15 mm;

(ii) transmittance of at least 20 % for ultraviolet light of 250 nm in wavelength; and

(iii) an angular half-width of not more than 100 seconds in an X-ray rocking curve in a (400) plane.

19. Vapor-deposited diamond comprising the following characteristics:

(i') a maximum diameter of at least 15 mm;

(ii') transmittance of at least 20 % for ultraviolet light of 250 nm in wavelength; and

(iii') a half-width of scattered light of not more than 2 cm^{-1} at a shift value of 1332 cm^{-1} from excited light in a Raman scattering spectrum.

FIG. 1

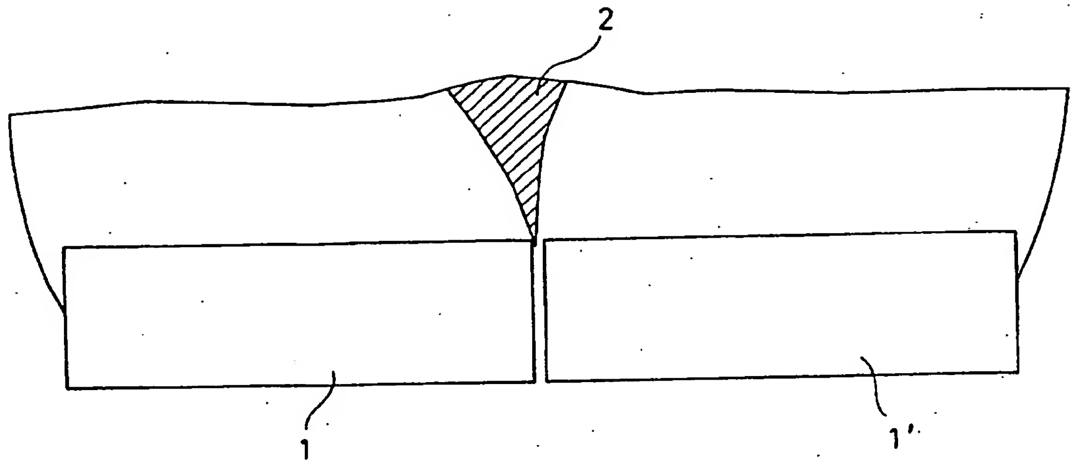


FIG. 2

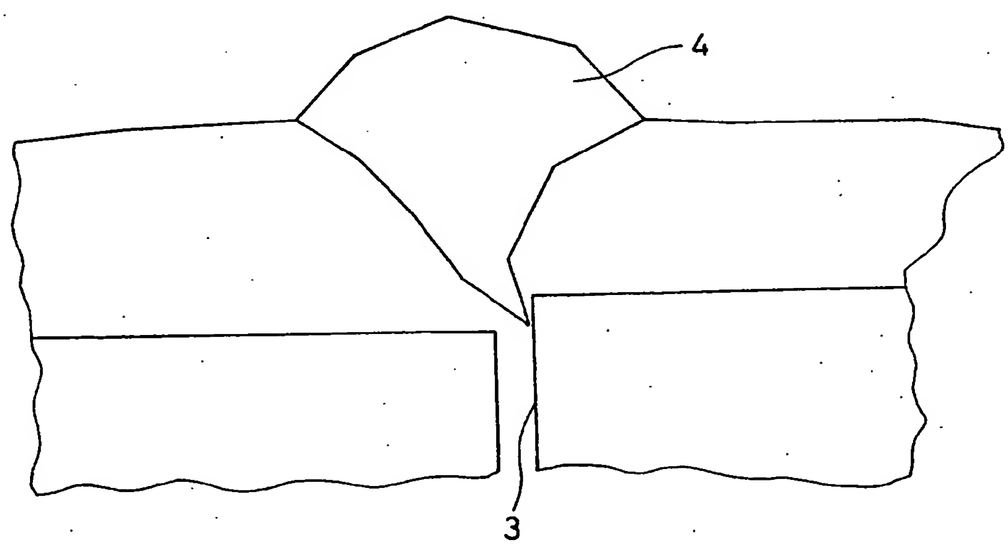


FIG.3

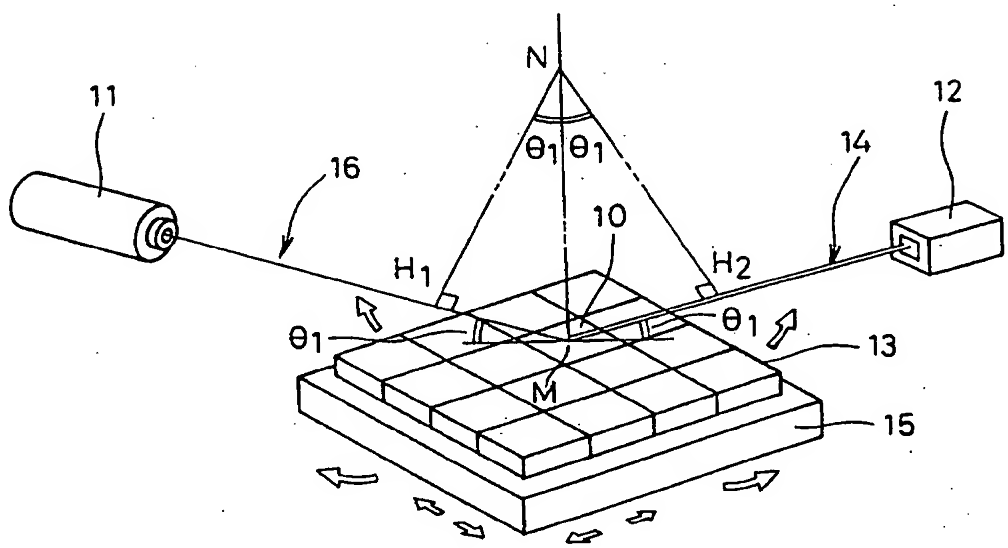


FIG.4

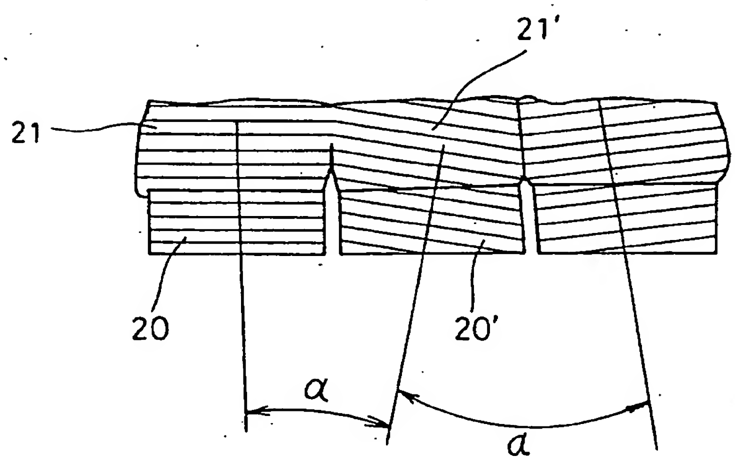


FIG.5

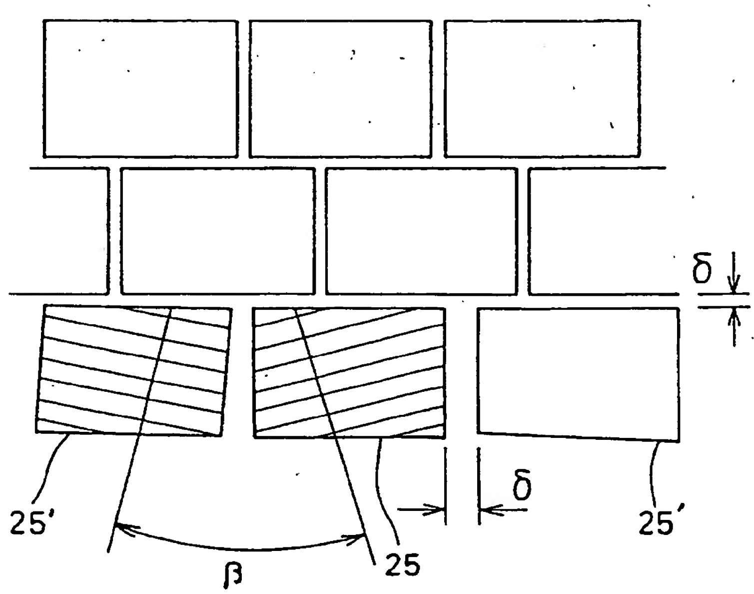


FIG.6A

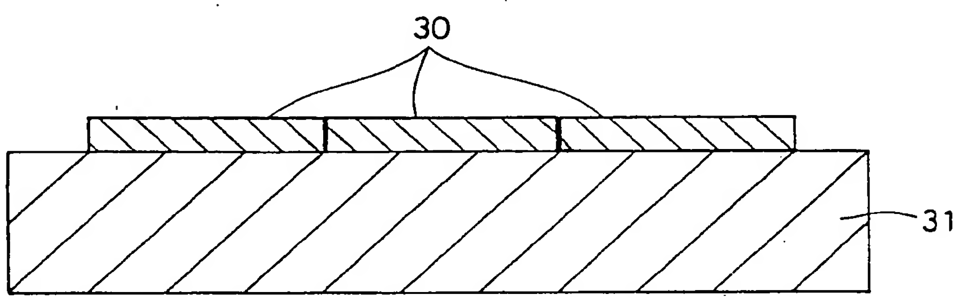


FIG.6B

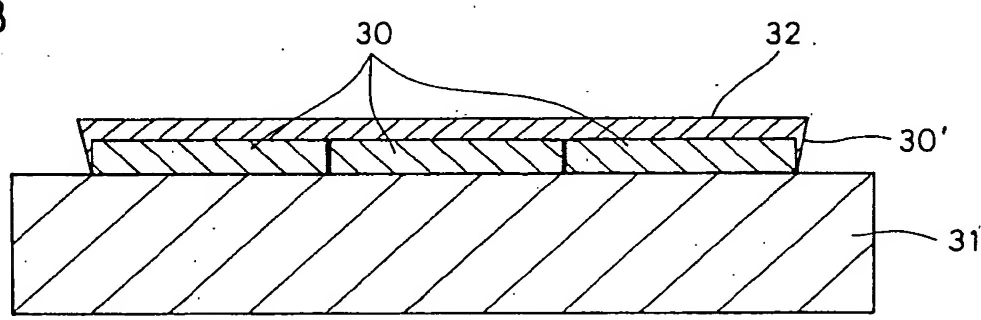


FIG. 6C

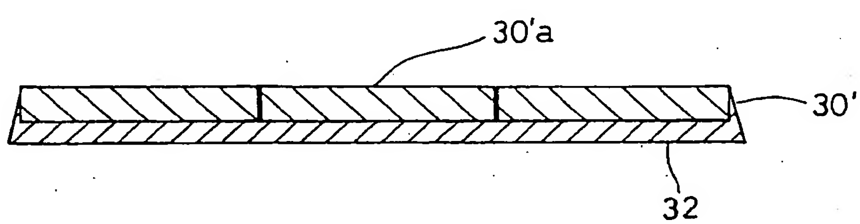


FIG.7A

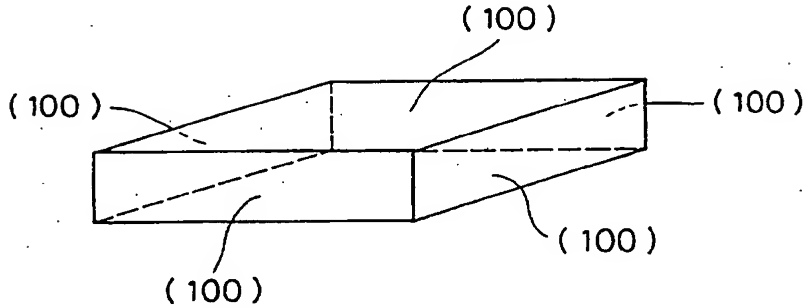


FIG.7B

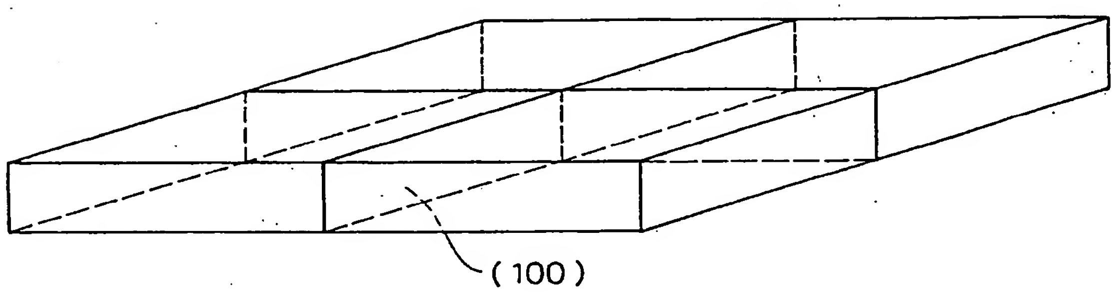


FIG. 8A

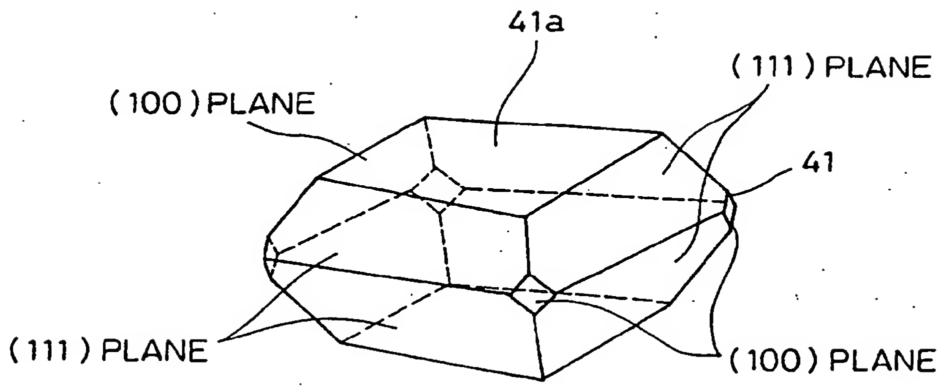


FIG. 8B

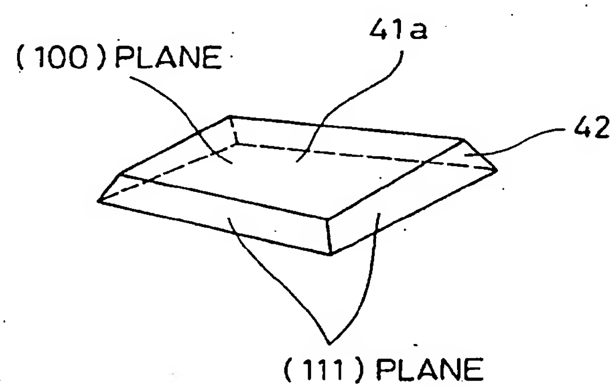


FIG. 8C

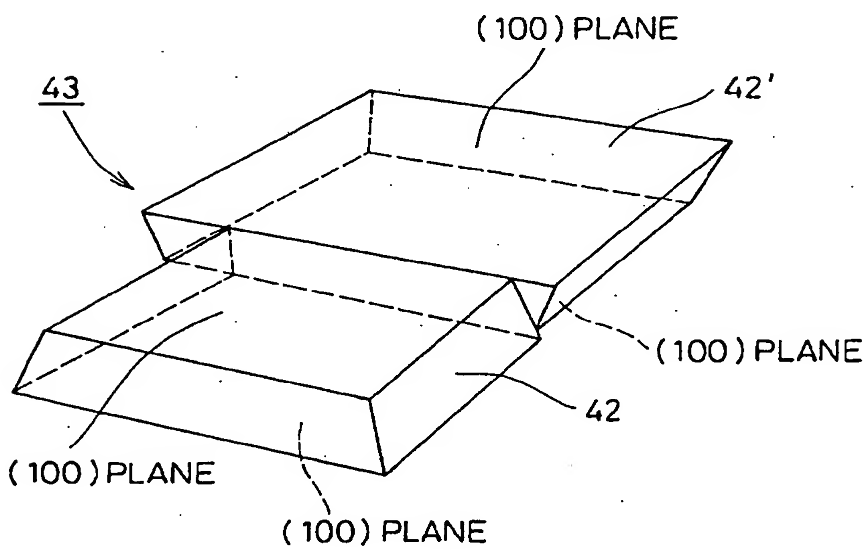


FIG. 9A

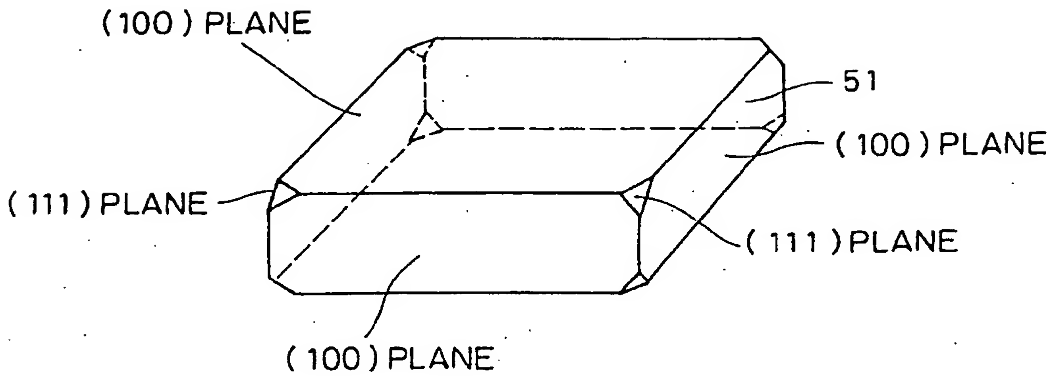


FIG. 9B

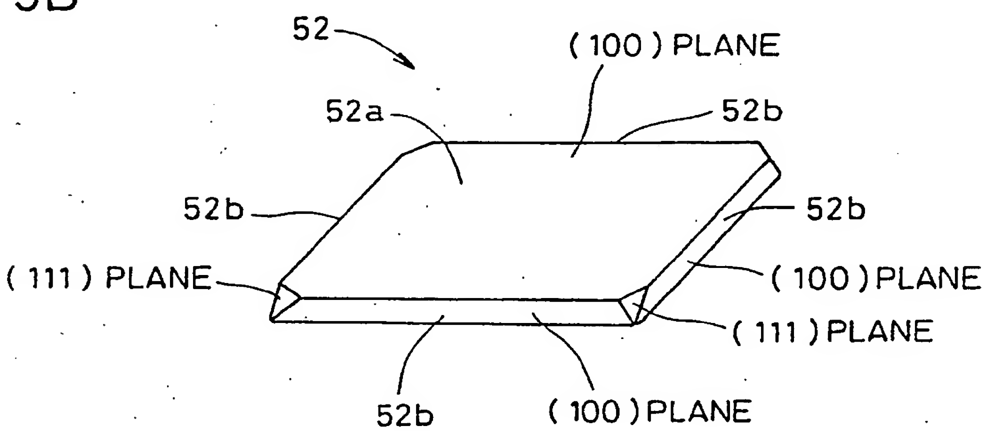


FIG. 9C

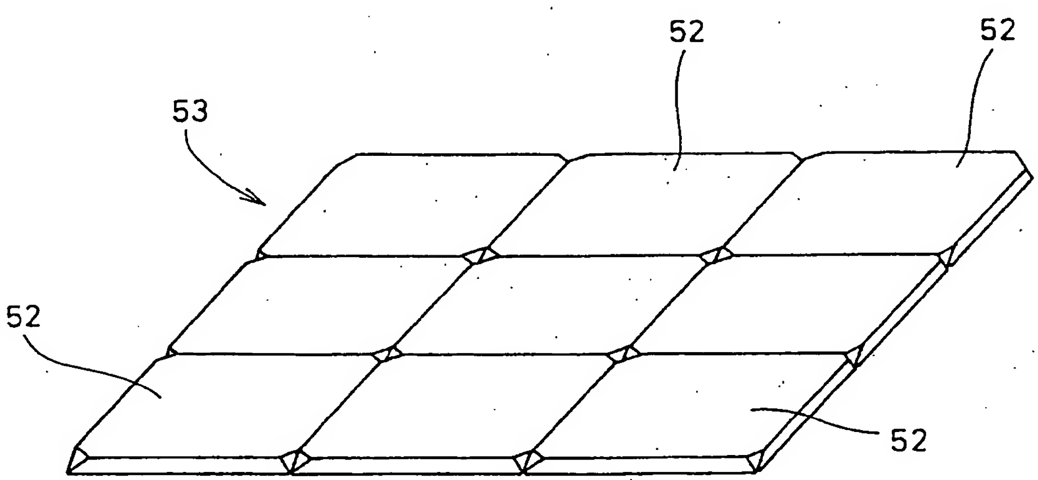


FIG. 10

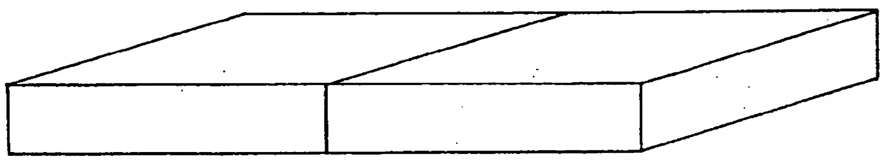


FIG. 11

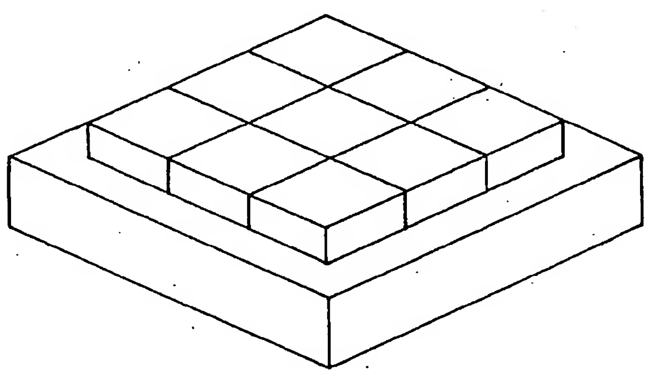


FIG. 12A

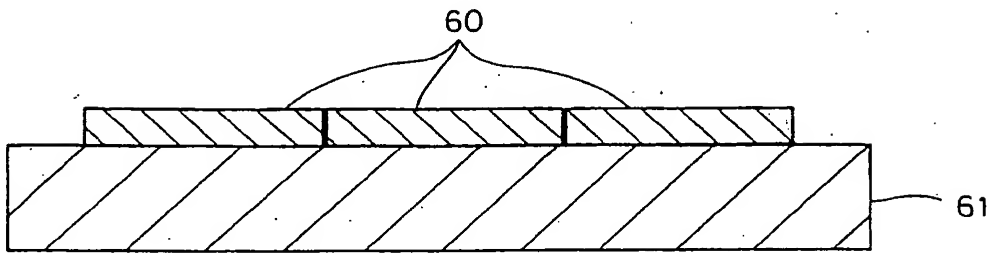


FIG. 12B

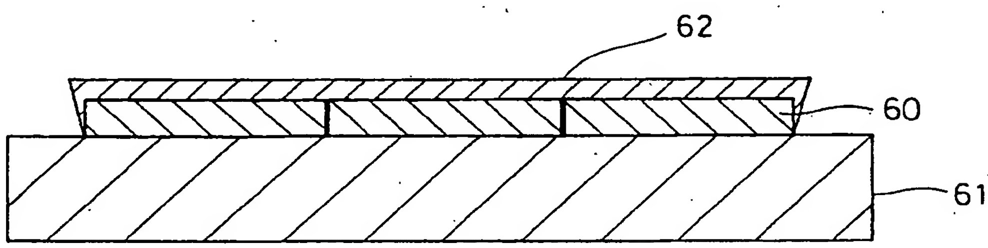


FIG. 12C

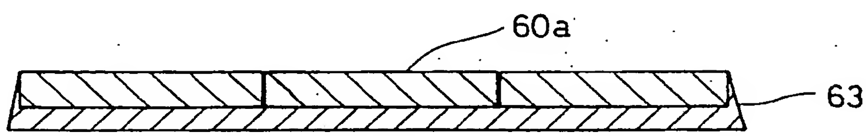


FIG. 12D

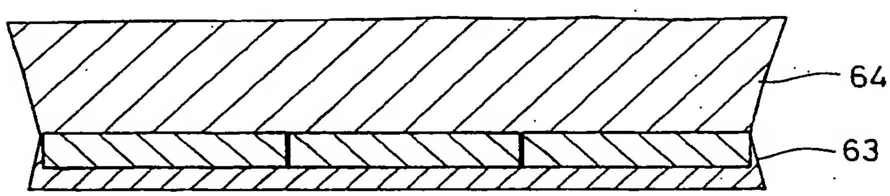


FIG. 13

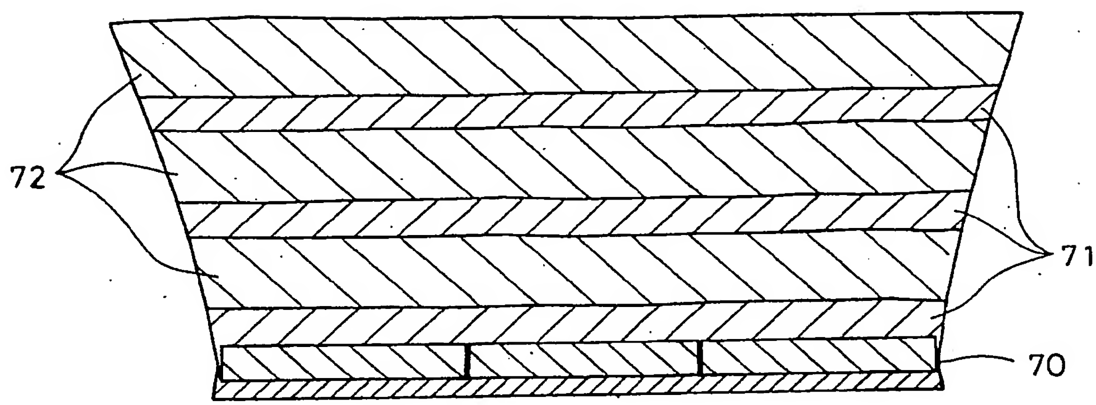


FIG. 14

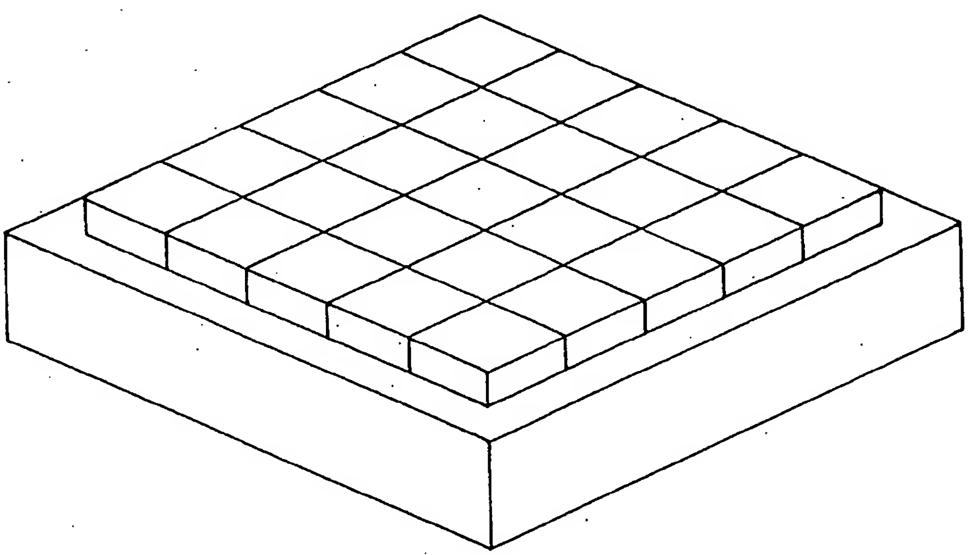


FIG. 15A

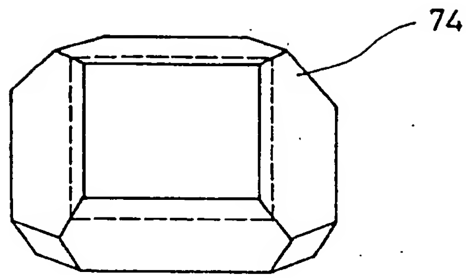


FIG. 15B

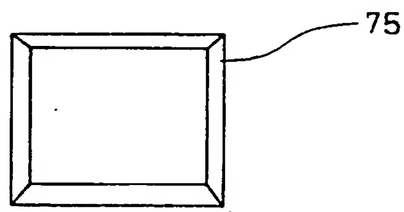


FIG. 15C

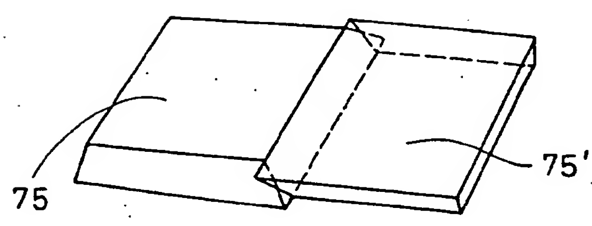


FIG. 16A

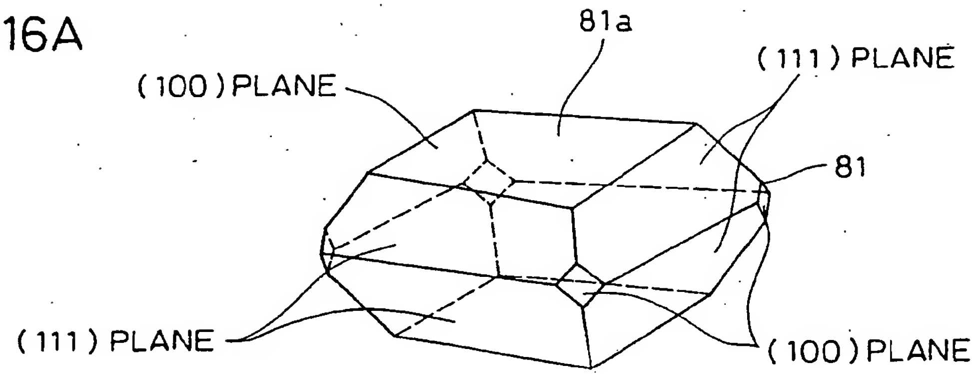


FIG. 16B

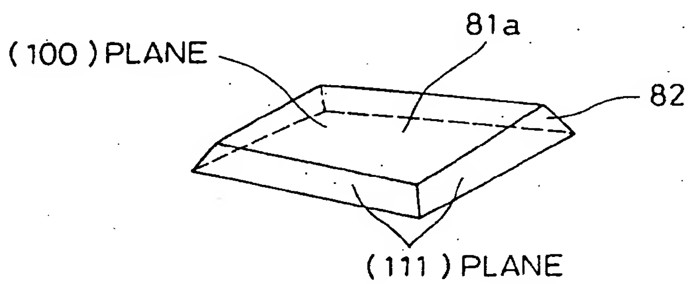


FIG. 16C

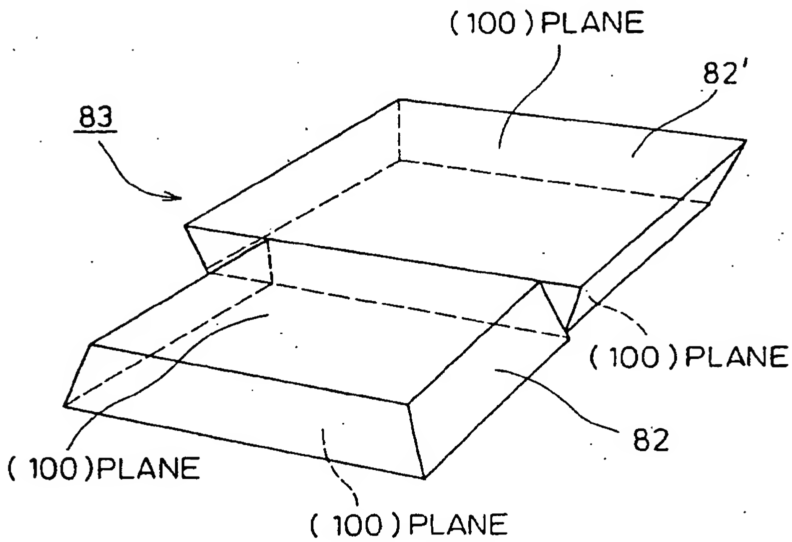


FIG. 16D

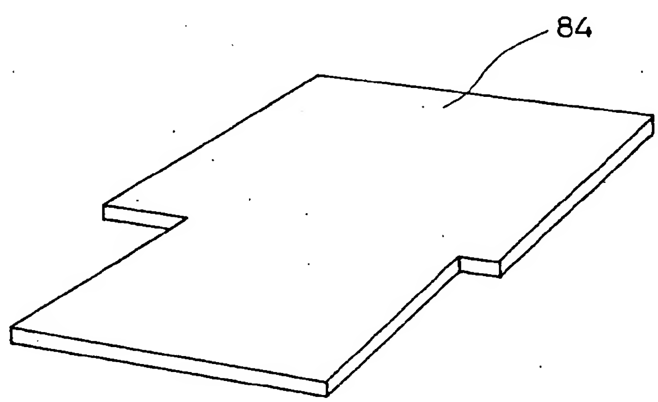


FIG. 17A

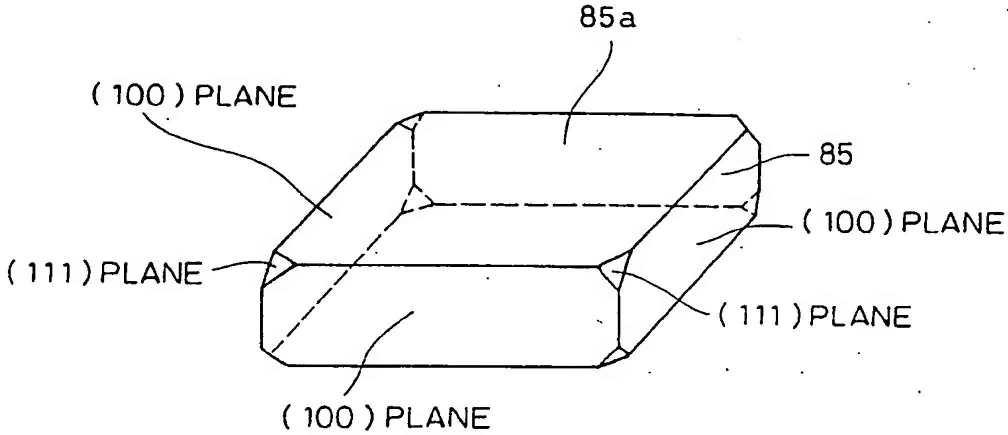


FIG. 17B

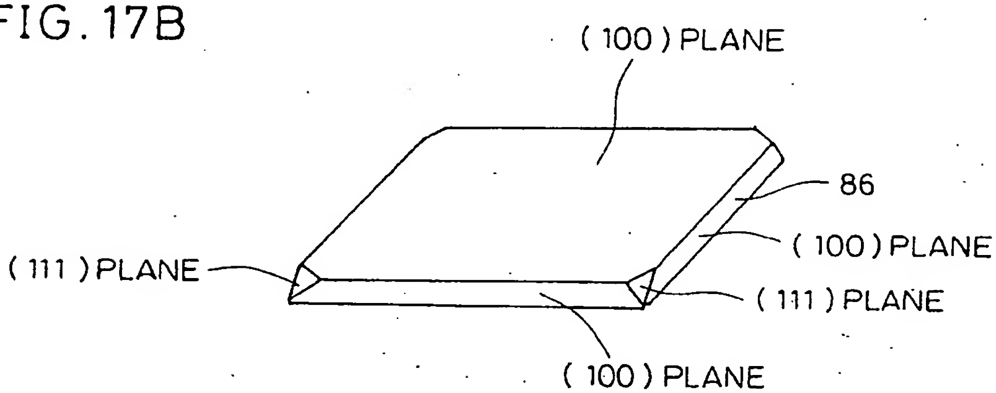
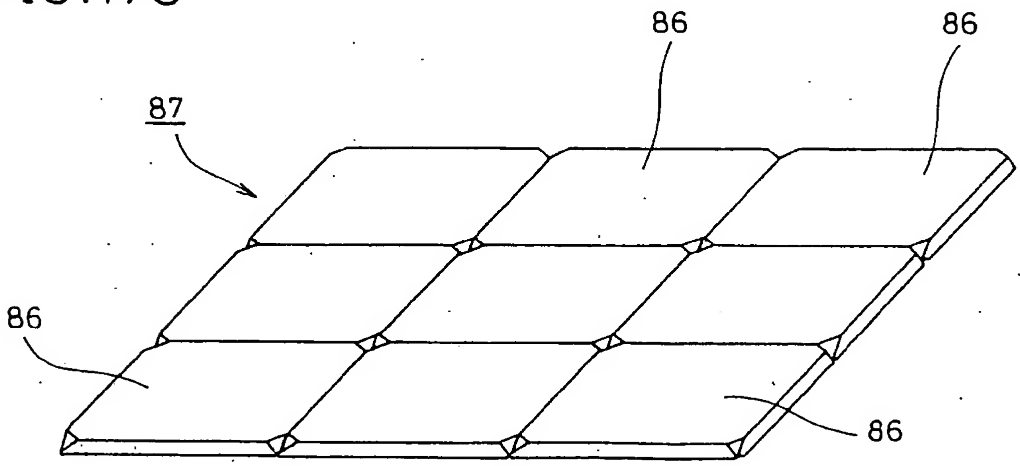


FIG. 17C



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93115385.2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,X	US - A - 5 127 983 (IMAI et al.) * Claims, examples * --	1,3, 13-15	C 30 B 29/04 C 30 B 25/02 C 23 C 16/26
A	EP - A - 0 487 897 (GENERAL ELETRIC COMPANY) * Claims; examples * --	1	
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 13, no. 61, February 10, 1989 THE PATENT OFFICE JAPANESE GOVERRNMENT page 123 C 567 * No. 63-252 999 * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C 30 B 29/00 C 30 B 25/00 C 23 C 16/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	10-12-1993	PAMMINGER

CATEGORY OF CITED DOCUMENTS

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